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(57) Abstract

A layered structure has superior properties because it is prepared by spraying two part liquid resin polymers that chemically react very quickly to become solid, to form each layer. A novelty is preparing all layers from a thermoset resin, which is possible because all layers are added by a spraying means. Structures are formed into articles such as boat hulls, truck liners, bathtubs, and automobile parts, using suitable molds. The articles have desirable properties such as durability, and relatively light weights. Moreover, they are produced more rapidly and inexpensively than similar layered articles produced by other methods.

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A LAYERED ARTICLE PREPARED BY SPRAYING THERMOSET RESIN TO FORM EACH LAYER

Background of the Invention

A layered structure has superior properties because it is prepared by spraying two part liquid resin polymers that chemically react very quickly to become solid, to form each layer. A novelty is preparing all layers from a thermoset resin, which is possible because all layers are added by a spraying means. Structures are formed into articles such as boat hulls, truck liners, bathtubs, and automobile parts, using suitable molds. The articles have desirable properties such as durability, and relatively light weights. Moreover, they are produced more rapidly and inexpensively than layered articles produced by other methods.

Layered articles have been prepared by a variety of methods using a variety of materials. The choice of materials and methods is dictated by the specifications of the structure of the specific article to be produced and by the availability of the compositions and apparatus available at a particular point in time.

Layered structures have been produced using thermoplastics, for example, which do not have as desirable properties as thermoset resins. The structures are less resilient, and the method of producing thermoplastic structures is lengthier and more costly than a method for producing layered structures from thermoset resins. Thermoplastics are polymers which soften under heat and are therefore amenable to molding by being injected or poured into cavities. Thermoplastics are not amenable to application by spraying.

Gel coat layers have been sprayed on inner cores prepared by methods other than spraying, but this tends to produce relatively heavy structures. Multilayered structures used for insulation have been described, for example, in JP 60,201,934, that have a foam core and thermoplastic resin outer sheets, but the design of this type of structure does not have to take into account damage to structural integrity, an important

consideration for articles such as boat hulls and automobile parts.

Multilayered sheets have been formed by extruding plastic (polypropylene and polystyrene) followed by thermoforming using a vacuum. See WO 8,302,747. Laminated structures have also been produced by injectional molding (EP 419829) and rotational molding as described in U.S. Pat. No. 5,096,652. In rotational molding, the laminate is made while the molded structure is being formed. Rotational molding has been used to produce boat hulls having three layers of polyethylene, with the middle or intermediate layer containing a foaming agent. U.S. Pat. No. 4,913,944. The layers are formed by particulate plastic being released into the mold cavity while the mold "rocks and rolls" in an oven, or at least goes in an oven at some point in the process. This process generally takes several hours, and requires a metal mold.

Fast-curing thermoset resins are relatively new compositions that form permanent and durable structures after being formed by heat or chemical reaction. Reactive injection molding (RIM) can be used with thermoset resins by injecting the mold cavity with the resins, but the result is not layered. Layered compositions have advantages of incorporating desirable characteristics of different materials into one structure, and even creating synergistic improvements over characteristics of the combined individual materials.

Thermoset polyesters, epoxys, polyurethanes, phenolics and other thermoset resins may be hand-layered, but this is time consuming and difficult due to the hand labor and the fact that some resins are slow setting. To increase tensile strength and stiffness, chopped glass fibres and foam may be added to layers. DE 3206468.

A method of applying a composition to a structure is spraying. Generally spraying will result in one layer of

a composition. However, spraying has been used to apply multilayers of polymers to wire strands, where the wire strands are layered within the layers of polymer. U.S. 4,891,086. Spraying has not been applied to produce layers of two part thermoset resins.

There are problems in production of multilayered structures and in the nature of the articles produced by the methods in the art. Problems include costs due to expense of preparation of molds suitable for the methods and compositions in the art, the length of time needed to prepare the structure, which increases cost and limits output, and difficulties in adapting to robotic manufacturing methods.

Therefore, there is a need to improve methods of preparing layered structures which could be quickly and inexpensively formed into articles such as boat hulls, automobile and furniture parts, bathtubs, truck liners to protect against abrasion and the weather, and the like. The improvements needed are to more quickly and efficiently accomplish the production of a more durable layered structure which is versatile in its applications. A goal of the present invention is to disclose and claim a method distinct from rotational molding, injection molding, blow molding, reactive injection molding, resin transfer molding (RTM), and extrusion molding, none of which have achieved the goals stated herein. It is another aspect of the present invention to teach how to produce a structure resulting from the method that is distinct from laminated plastic sheets, including those with foam cores, and from structures that were not bound to each other by chemical reactions between the layers. The structure of the present invention has layers that do not dissociate.

Summary of the Invention

A layered structure with superior properties is prepared by spraying a two part thermoset resin to form layers. The structure is moldable into various articles

such as boat hulls, automobile and furniture parts, bathtubs, and truck liners. The articles formed from the layered structure of the present invention are more durable, resilient, lightweight, and inexpensive, than are comparable articles produced by other methods and compositions.

The present invention is directed to a method for making a layered structure, where there may be from 1 to n layers. A structure that has two or more layers is called a "multilayered" structure.

The method includes the following steps:

a. Selecting a composition for a first layer.

The composition of the first layer is selected depending on criteria dictated by the type of article to be produced. The composition and structure of the first layer of a structure is determined by the specification for a particular application. In various illustrative embodiments, the first layer may be composed of a resin, for example a two-part thermoset resin. Thermoset resins that are suitable for use in the present invention include resins that are characterized by elongation of at least 10%, and that are suitable for spraying. In a preferred embodiment, the resin is an elastomer, that is, a composition with a very high elongation, for example, 100%. Thermoset polymers (resins) when molded to a specific shape cannot be subsequently softened. Compositions that are suitable for the purposes of the present invention include polyurea and a mixture of polyurethane and polyester.

An advantage of fast-curing thermoset resins for the present invention is that the two-part resins harden or set very quickly after they are mixed and form very durable structures. By quickly is meant within, for example, seconds or minutes as compared with hours needed for some compositions in the art used for pour molding, resin transfer molding, and injection molding to set. For example, a thermoset resin formed of polyurea hardens

or sets to form an article, within about 3-40 seconds, as compared with polyethylene used in rotational molding, which may require at least one hour to form an article, and some other compositions that take 8 hours to set, especially if the goal is to produce a multilayered article.

In a multilayered structure of the present invention, the layers may all be of different compositions, or may be of the same composition, or any combination thereof. In an illustrative embodiment, the composition of at least one of the layers other than the first layer, that is, a layer which forms an inner (intermediate, middle) layer of a multilayered structure, may be a foam layer. In an illustrative embodiment, the foam layer is made by mixing a blowing agent such as water with the resin layer. The water reacts with isocyanide to form carbon dioxide which introduces bubbles into the resin, to form a foam. An advantage of using the same basic composition in all layers, is to minimize delamination (undesirable separation of the layers) caused by differential response of layers of different compositions to the environment.

There may be any number of layers in the layered article, from 1 to n. The upper limit is dependent on the applications for which the structures are to be used. In a preferred embodiment, there are three layers composed of an outer and an inner resin layer (or substrate), and an intermediate foam layer. This type of structure, which may be referred to as a "sandwich", is useful for forming into an article such as a canoe. Where there are layers beyond three, generally at least the inner and outer layers are solid resins, rather than foam. Generally, foam and solid layers will alternate. However, any combination of semi-solid or solid resins are within the scope of the present invention.

b. Spraying the composition onto a suitable support to form a layer.

The first layer is designated as the layer that is emitted from a spraying apparatus first during the process of making the layered article. Generally, the first layer will constitute the outer layer (substrate) of the finished article. The first layer is sprayed onto a solid support. The solid support is generally a mold, but may be any solid support that allows the first layer to harden in a manner suitable for a particular application. The solid support in the form of a mold, form or other suitable type, need not be prepared to a specific temperature, as are such supports used for other methods in the art. A suitable ambient air temperature is in the range of 60-150.

If pigments are to be added to a molded product, they are usually added to the mold prior to the first layer as paint, or are added to the first layer, or both. If the article is to be exposed to ultraviolet light, the first sprayed layer may contain an ultraviolet resistant paint, generally in a layer of about 1 to 4 mil thick. This procedure is referred to as "in mold painting."

The spraying of the resin to form layers is accomplished by any apparatus that is capable of distributing a thermoset resin, or a comparable composition, into a layer. Examples of spraying apparatus include manually operated spray guns, a plurality of spray guns operated sequentially, a spray gun with multiple nozzles, a single spray gun used repeatedly, or a robotic spraying apparatus. The robotic method is likely to produce more desirable thickness in layers than a manually controlled spraying apparatus.

c. Repeating step a and b as many times as required to form the multilayered structure.

As mentioned in parts a and b, the first layer is generally sprayed onto a solid support that is provided initially, for example, a mold. An advantage of the present invention is that the mold does not have to be heavy, resistant to extreme temperatures, or have complex

and tight closing means. In fact, a mold may be made of the same resins used for the layers of the structure produced by methods of the present invention.

Subsequent layers use as their solid support, a previously sprayed layer. The second layer may be sprayed after the first layer sets up, although spraying of subsequent layers could wait for a long time, as long as no contaminants, such as oil or silicone-laden air, affect the surface.

The second sprayed layer is sprayed onto the first layer, wherein the second layer adheres to the first layer. The third sprayed layer is sprayed onto the second layer, and so forth. This process is repeated until all layers required for a particular article are sprayed. Other materials, such as metal reinforcements or ribs, may be incorporated into the layers.

An article is defined as any structure which is formed from a layered structure, wherein the layers have been formed by the methods of the present invention. The term "article" includes both formed and unformed structures wherein "formed" includes structures shaped into recognizable shapes and "unformed" includes structures that are not useful without further processing.

The methods of the present invention are suitable to make any multilayered article including a boat hull, such as a canoe hull, a liner for a truck receptacle, automobile parts such as fenders, and furniture.

Advantages of the present invention include quick, therefore, more efficient means of producing multilayered articles. Cost is reduced because production time is dramatically reduced, and the only apparatus required is a spraying apparatus. The mold does not have to be heated prior to spraying, and may be comparatively inexpensively and simply constructed.

An important advantage for the environment resulting from using fast-setting resins is that less contaminants

escape, e.g., isocyanate, due to a reduced time during which compositions are volatile.

An aspect of the present invention is the layered structure formed by the method disclosed. The structure is composed of one or a plurality of layers, depending on the nature of the application of the structure. A suitable composition of the first layer of the structure includes a thermoset resin. A suitable composition of at least one of the inner layers of the suitable includes a foam, for example, a foam composed of water and resin. The resin is a thermoset resin. There is no size limitation associated with an article produced by the methods of the present invention, although it is most suitable for relatively large articles, such are exemplified herein.

The advantages of the layered structure of the present invention include flexibility of construction and of composition of the layers. The layers may be thicker or thinner in areas where a thicker or thinner thickness is advantageous, in contrast to what can be achieved using other methods, for example rotational molding or blow molding. If robotic spraying is used, layer thickness is controlled. Additives may be put in the layers such as pigment, and metal reinforcements. Another advantage is that when used for a molded article, the composition applied by the methods of the present invention, has a "mold memory," rather than a sheet memory as in the methods of the art which heat sheets and mold them into forms. Thermoplastic type compositions are characterized by a tendency to revert to their original form from a subsequently imposed form, such as that imparted by the thermo-formed molding process. Therefore, articles of the present invention are more responsive to repairs especially after being damaged, for example, by blows to the article.

The layers of the structure may be any thickness, but a preferred range is from 2-40 mil. Layers may be the

same or different thicknesses when compared to each other. Layers of the same composition may be accumulated to increase the thickness of a particular composition layer, e.g., from to 40 mil to 2 inches. The number of layers will be a function of the thickness of an individually sprayed layer, and the number of repetitions.

Detailed Description of the Preferred Embodiments

Thermoset Resins

Thermoset resins are suitable for the methods of the present invention if they are capable of being applied to a solid support by spraying, and they have an elongation of at least 10 %. The resins are two-part liquid resins of polymers that chemically react very quickly to become solid. By a two part resin is meant a composition which is divided into two components which must be mixed in order for hardening to occur. By very quickly is meant in as little time as seconds. The exact hardening time will vary with the specific composition.

In an illustrative embodiment, the resins comprise polyurea. In another embodiment, the resins comprise a hybrid polyurethane and polyester. A suitable composition is the EC Series 23, which is available from EniChem, Polyurethane Design Division, 1448 V.F.W. Drive, Conyers, Georgia 30207. Characteristics of the EC Series 23 are shown in Table 1. EC Resin System Series 23 is a 100% solid polyurea system. It has been used for reaction injection molding(RIM). For that purpose, key processing benefits are the adjustable gel time from 3 to 45 seconds, which was purported by the manufacturer to eliminate mold flowing problems. "Fillers" are easy to process for enhanced properties; "optional internal molding release" is available for optimizing cycle times.

The EC23 system enhances the quality of the molded part by minimizing sink marks and shrink. Also, paintability is said to be excellent using standard automotive paint and techniqu s.

TABLE 1: Characteristics of EC Series 23

PHYSICAL PROPERTIES:

	EC 23-21	EC 23-25
Specific Gravity	1.12	1.120
Thickness	.125	.125
Tensile Strength PSI	3.5K	3.9K
Elongation %	95	73
Flexural Modulus PSI	80K	100K
Shore D	600	65D
Notched Izod-Impact	7	5
Linear Shrinkage	0.75	0.75
Heat Sag-1 hr. @ 250°F		
4" Overhang	____	____
6" Overhang	____	____

MOLDING CONDITIONS

ISO Temperature	90°F	90°F
Polyol Temperature	90°F	90°F
Mixing Pressure	2000 PSI	2000PSI
Mix Ratio	1.14/1PBW A/B	1/1PBW AB

Another resin suitable for use in the present invention is the EniChem series EC 242. Characteristics of that series of resins are presented in Table 2. EC Resin Systems Series 242 is a high-modulus hybrid polyurea that was designed for high productivity RIM production. Gel times are adjustable from 5 to 45 seconds implemented by catalyst changes. According to the manufacturer, EC 242 provides excellent green strength and good release characteristics from the mold. EC Series 242 has excellent impact strength with minimal heat sag up to 275°.

TABLE 2: Characteristics of EC Series 242

PHYSICAL PROPERTIES:

	EC 242-21	EC 242-25	ASTM Method
Density	68PCF	68PCF	D 1622
Hardness, Shore D	72	75	D 2240
Tensile Strength	5300 PSI	5900 PSI	D 412
Elongation @ Break	180%	140%	D 412
Flexural Modulus @ 22°C	150,000 PSI	223,000 PSI	D 790
Heat Sag, 4" overhang			
1 hr. @ 121°C	—	—	D 3769
1 hr. @ 121°C	.13 ins.	.13 ins.	D 3759
Notched Izod Impact	75. ft/lbs.	6 ft./lbs.	

** Post Cured @ 121°C for one hour

Spraying Means

Any means for spraying a two-part thermoset resin on to a solid support so that the resin forms a layer, is suitable for purposes of the present invention. A spray gun may be ordered from Tel 908 Gusmer, 1 Gusmer Drive, P.O. Box 110, Lakewood, New Jersey 08701-0110. Apparatus for spraying include the gun claimed in FR 2520639; and the thermal spray gun of U.S. 4,999,225.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of examples. It should be understood, however, that it is not intended to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

EXAMPLE 1: Preparation of a Three-Layered Structure

The first layer was composed of thermoset resin EC 491. It was sprayed on to the solid support using a spray gun and allowed to harden for one minute. A solid support was a fiberglass canoe mold.

The second layer was a foam layer produced by adding water to the non-isocyanate part of the resin system Part B. When the two parts are mixed, the water reacts with the isocyanate in Part A to form CO_2. The more water that is added, the more CO_2 that is produced, and the more foaming action, or less density, results. The second layer was sprayed on to the first and allowed to harden for two minutes.

The third layer was composed of the same resin used in the first layer. It was sprayed onto the second layer and allowed to harden for 45 seconds.

The thickness of the first and third layers was about 50 mil or .050 inches.

The temperature at which the spraying was done was 72°.

EXAMPLE 2: Producing a Canoe

The three layered structure of Example 1 is used to form the structure of the canoe.

The solid support used was a canoe-shaped mold. The mold that was used is a hand layed-up polyester fiberglass mold, the same type of mold that is used for a hand layed-up boat, such as a canoe or other fiberglass structure.

A mold is made using the same equipment and the same basic material as described in Example 1. This means a part can be duplicated by waxing the part, spraying the support as described in Example 1 (to create a mold), pulling the part from the mold, waxing the mold, spraying the mold again as in Example 1, to duplicate the part.

EXAMPLE 3: Manufacturing a Liner for a Truck Cavity

A liner that fits snugly into the cavity of a truck is desirable to protect the basic truck finish from abrasion, for example, due to articles transported in the